LA-UR-22-31673

Approved for public release; distribution is unlimited.

Title: Nuclear Forensics: Identification and Characterization of Materials Outside of Regulatory Control

Author(s): Steiner, Robert Ernest
Lamont, Stephen Philip
Tenner, Travis Jay
Inglis, Jeremy David

Intended for: General overview for students

Issued: 2022-11-03

Los Alamos NATIONAL LABORATORY

Nuclear Forensics: Identification and Characterization of Materials Outside of Regulatory Control

Robert Steiner, Stephen LaMont, Travis Tenner and Jeremy Inglis
Los Alamos National Laboratory

08 November 2022

Managed by Triad National Security, LLC, for the U.S. Department of Energy's NNSA.

LA-UR-22-XXXXX

Outline

- Introduction
- Contamination Control
- Instrumentation
- Radiochonometry
- Spatially Resolved Analysis
- Future Focus Areas

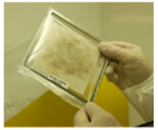
Nuclear Security Programs Across the Pre- and Post-Detonation Spectrum

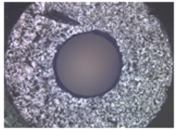
Prevent

Nuclear Nonproliferation
- Nonproliferation treaty compliance
- IAEA Environmental Safeguards Lab (NWAL)

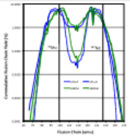
R&D to improve detection of undeclared activities

Nuclear Test Monitoring
- Nuclear test ban treaty compliance
- Nuclear Debris Collection and Analysis (NDC&A)





Materials Measurement Nuclear Security Programs



Respond

Pre-det Nuclear Forensics
- Operational samples
- US National Nuclear Forensics Library support
- International engagement and capacity building

R&D to identify signatures and improve timelines

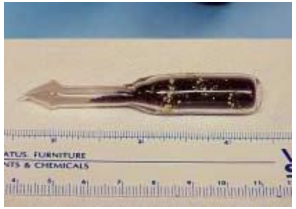
Post-det Nuclear Forensics
- Analysis of ground and air particulate debris
- Debris diagnostics
- Material attribution and design provenance

Pre-detonation

Post-detonation

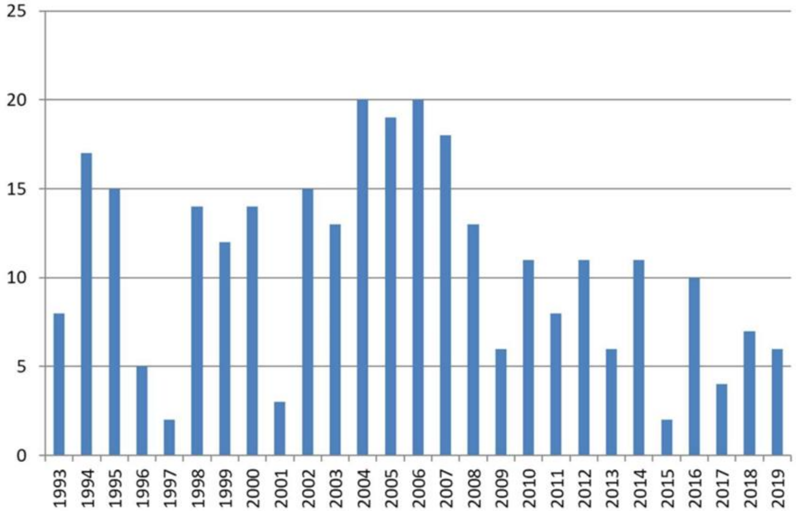
Nuclear Forensics: Investigating Incidents Involving Material out of Regulatory Control (MORC)

3686 incidents since 1993



290 with malicious intent

Incidents related to trafficking or malicious use1993 - 2019[1]



1023 with unknown intent

[1]2020 IAEA Incident and Trafficking Database Factsheet

[2] The Guardian, Nuclear Smuggling: Large Rewards Tempt Desperate and Poor into Trade

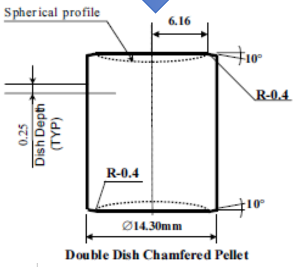
[3] Reuters Photo, The Guardian “Nuclear Smuggling, the Expert View

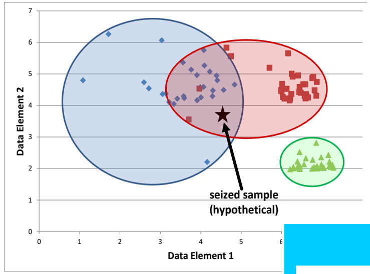
Nuclear Forensic Science

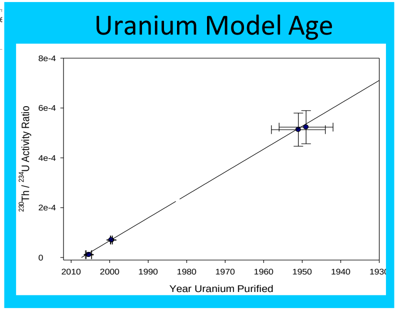
- *Nuclear forensics* is the collection and analysis of nuclear or radiological material to support investigations into the diversion, trafficking, or illicit activities involving materials

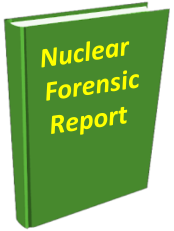
  - What is the material?
  - What was its intended use?
  - How was the material produced?
  - When was the material last processed?
  - Where is the material used, produced, or stored?
  - Who is associated with a material?

Goal: Link nuclear or radioactive material to people, processes, events and/or locations









Los Alamos NATIONAL LABORATORY

Nuclear Forensics Part 1: Evidence

Part 1: Traditional Forensics:
Link individuals to criminal activity

Material Analysis

Judicial Proceedings

Trafficker Convicted

- Important for judicial proceedings
- Requires high-quality, legally defensible analyses
  - What is it?
  - How much is there?
- Does not require a detailed analysis of all material attributes
- *Signatures generally do not play a large role in evidence for judicial proceedings*

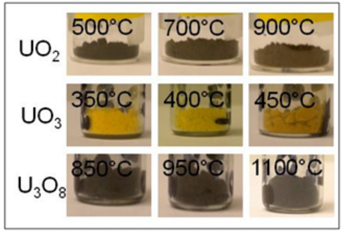
Nuclear Forensics Part 2: Investigations

- Detailed analysis of material attributes
- SME data interpretation
- Assessment of material process history and provenance
- Connecting material to people, places, and other materials
- *Signatures play a key role in answering investigative questions and generating investigative leads*

Part 2: Investigative Forensics:
History of nuclear material

Full Characterization
- Precision isotopics
- Chemical composition
- Age dating
- Morphology

Comparative Analysis & Signature Evaluation
- Intended use
- Process history
- Fuel cycle information



Outcome
- Possible origins
- Connections between cases
- Enhanced security

Los Alamos NATIONAL LABORATORY

1999 Bulgaria 73% HEU Example

Non-nuclear forensics

- Wax type
- Wax colorant
- Paper origin
- Pb metallurgy
- Pb isotopics
- Ampoule material

Nuclear material forensics

- Particle characterization
- Stoichiometry
- Impurity elements
- Residual radionuclides
- Age-dating
- U & Pu isotopics

LLNL-Led Effort: Excellent demonstration of what could be done!

National Nuclear Forensics Libraries

- If nuclear material is found outside of administrative controls anywhere in the world, then each country should be able to answer the question:

  "Is this consistent with material used, produced or stored within our borders?"

- IAEA guidance and good nuclear security practice recommends each country has a responsibility to identify their materials, should they be found out of regulatory control

A ***national nuclear forensic library (NNFL)*** is extremely valuable for answering this question with timeliness and confidence – it can also help investigators answer investigative questions regarding material production history and provenance

Which characteristics, for which materials, can answer which investigative questions?

Investigative Questions

What is the material?
Intended use?
Fuel cycle association?
Production process?
Last purified?
Connection to other cases of MORC?
Connections between bulk and trace evidence?
Is it from our inventory?

Materials

UOC
UF_6
DU
UO_2
Fuel
Spent Fuel
Reprocessed U
PuO_2
U Metal
Pu Metal

Characteristics

Dimensions
Density
Particle Size
Specific Surface Area
Chemical Form
Crystallography
Elemental Composition
Trace Elements
Isotopic Composition
Radiochronometry
Heterogeneity

Through the forensic examination of known materials and cataloging characteristics, we are better prepared to develop efficient analysis plans to answer investigative questions for real cases.

Material Characteristics & Investigative Questions

- Which material characteristics are useful is tied to the question being asked
- Value of forensic characteristics is dependent on context
- *Forensic examination analysis plans should be designed to answer investigative questions*

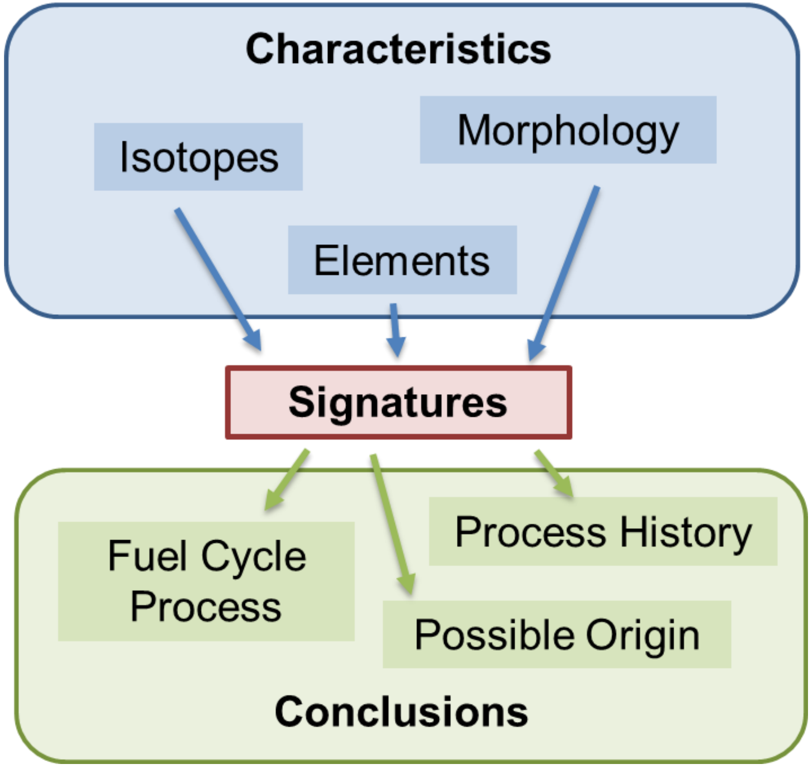
Q1: Is this LEU oxide powder from a LWR fuel production plant?

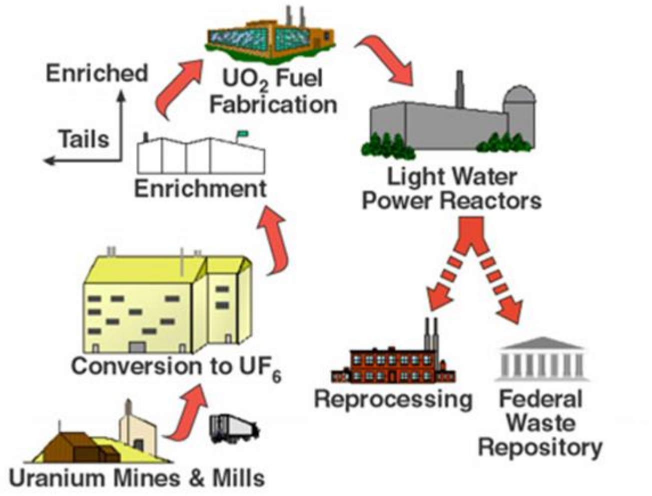
Q2: Is this LEU oxide powder from the LWR Fuel Plant X or Fuel Plant Y?

Characteristic	Analysis Result	Discriminating Signature?	
		Q1?	Q2?
Chemical form	UO_2	Yes	No
Enrichment	4.3% ^{235}U	Yes	No
Trace elements	20 ppm Mo	No	Yes

Los Alamos NATIONAL LABORATORY

Nuclear Forensic Signatures: Connecting Material Characteristics to Provenance





Investigative nuclear forensics requires a better understanding how characteristics are created, changed, and lost as materials transit the fuel cycle

Advancing the state-of-the-art for nuclear forensics

- Policy drivers for nuclear forensics R&D

Law Enforcement
- Examining evidence and presenting defensible data

Investigative Assistance
- Establishing links between people, places, materials, and events

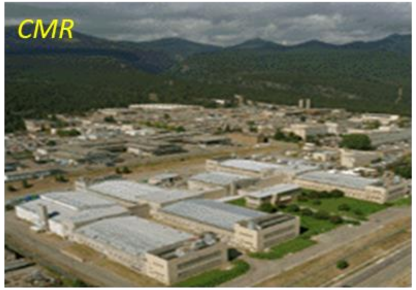
National Nuclear Forensics Libraries
- Nuclear security need to identify material provenance

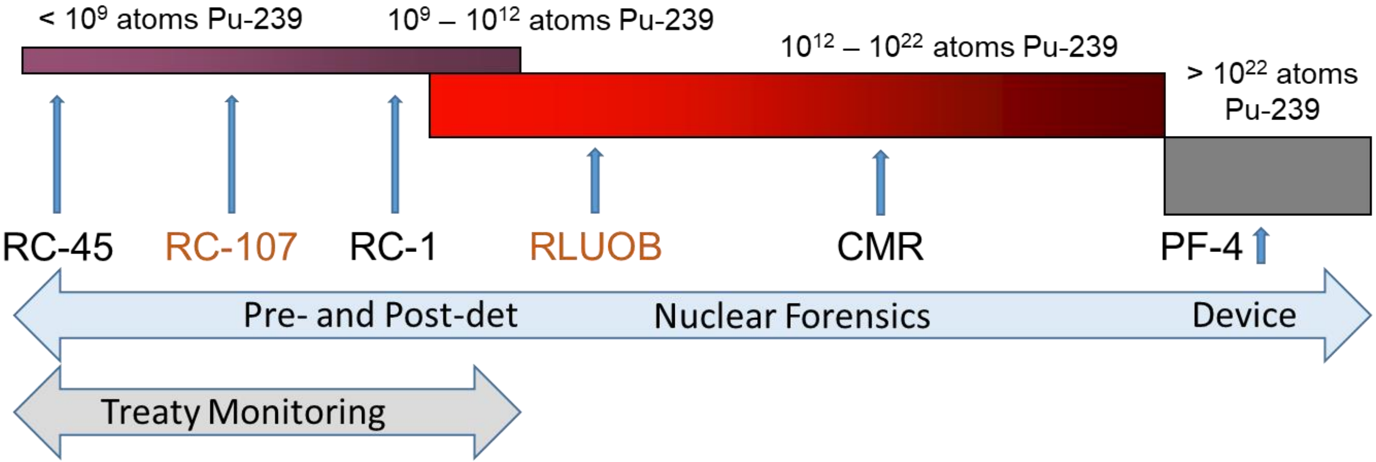
Measurement Science
- Accuracy, precision, and defensibility of measurements
- Investigating new techniques with applications to forensics

Understanding Signatures
- How characteristics are imparted on materials throughout the fuel cycle
- Which characteristics are useful for answering which investigative questions

Radiochemistry Facilities

All facilities house ongoing missions that exercise analytical capabilities routinely





Contamination Control

Contamination risk from finely divided powders of α-emitters is significant

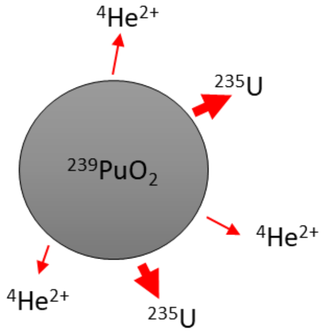
NDA confirmed WGPu in CMX-6, likely in the form of a finely dispersed powder

Common materials and risk

Specific Activity ↑ / Contamination Risk ↑

- ^{238}Pu: 6 x 10^{11} Bq/g
- RGPu: 2 x 10^{9} Bq/g
- WGPu: 1 x 10^{9} Bq/g
- HEU: 2 x 10^{6} Bq/g
- LEU: 1 x 10^{5} Bq/g
- NAT U: 2 x 10^{4} Bq/g
- DU: 1 x 10^{4} Bq/g

Alpha Decay



The combination of recoil nuclei and electrostatic interactions can disperse particles of high-specific activity materials

Los Alamos NATIONAL LABORATORY

Strategies for working with high-specific activity particulate samples

Glovebox

- Best option for health and safety
- Usually a requirement for gram or larger quantities of particulate Pu
- *Difficult to keep clean*

Fume hood

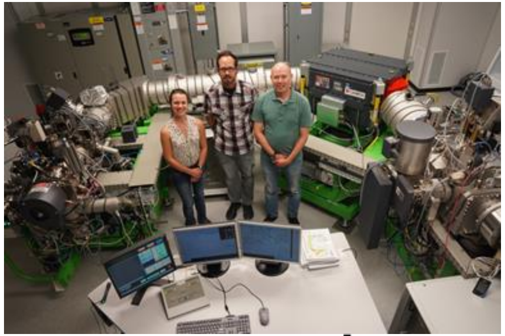
- Usually okay for mg quantities of Pu and all U
- *Much easier to keep clean than glovebox*

Glovebag inside of a glovebox or fume hood

- Glovebags are generally not considered engineered barriers
- *Prevents facility–to–sample cross contamination*

C-NR Instrument Capabilities

Multi-collector ICP-MS
(MC-ICP-MS)
High precision, high accuracy
Isotope ratios (U, Th, Sr, Pb, Fe, B…))



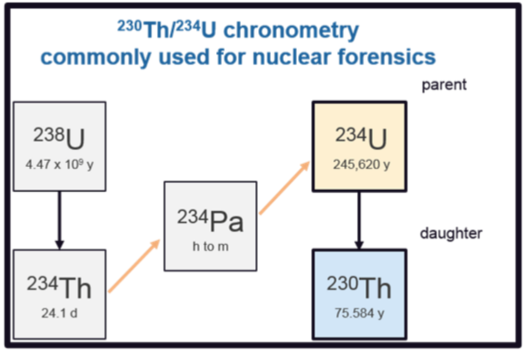
Multi-collector SIMS
Particle analysis

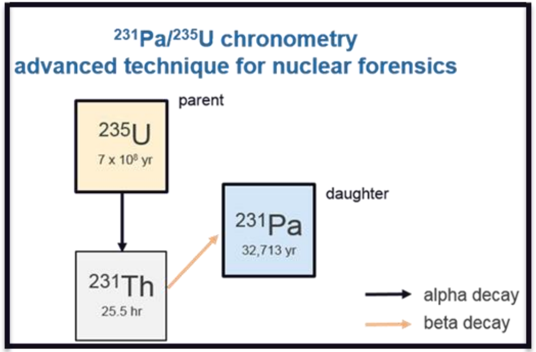
Sector Field ICP-MS
(SF-ICP-MS)
ppq – ppm element conc.and some isotope ratios

Multi-collector TIMS
Pu, U, Am, Np, Sr, Nd, others

Other instrumentation
XRD, XRF, SEM, LA-LIBS

Radiochronometry – Nuclear Forensic Signature





Use of radioactive decay chains to date the time of last chemical purification of U or Pu materials

Model age of a radioactive material out of regulatory control can be used as a *predictive* or *comparative* nuclear forensic signature

Facility A
operated 1950 - 1970

^{230}Th/^{234}U
production date
May 1995

Facility B
operated 1990 - present

Is a radiochronometry model age consistent with facility production history?

Are radiochronometry model ages of pellets consistent with each other?

Pictures from www.world-nuclear.org, vector graphic, and US Nuclear Regulatory Commission

Important Assumptions

- Radiochronometry provides a “model age”
  - Assumes complete parent / progeny separation at t_0
  - Assumes a closed system

- Multiple chronometers may not give the same model age
- Discordant chronometers can provide insights into process history

Simplified ^{234}U-^{230}Th Age Equation

$$t_{(years)} = \frac{1}{\lambda_{234U} - \lambda_{230Th}} * \ln\left[\frac{R(\lambda_{234U} - \lambda_{230Th})}{\lambda_{234U}}\right]$$

$R = {}^{230}Th/{}^{234}U$ atom ratio

$\lambda_{234U} = 2.83 \times 10^{-6}$

($T_{1/2}$ = 245,250 (490) years)

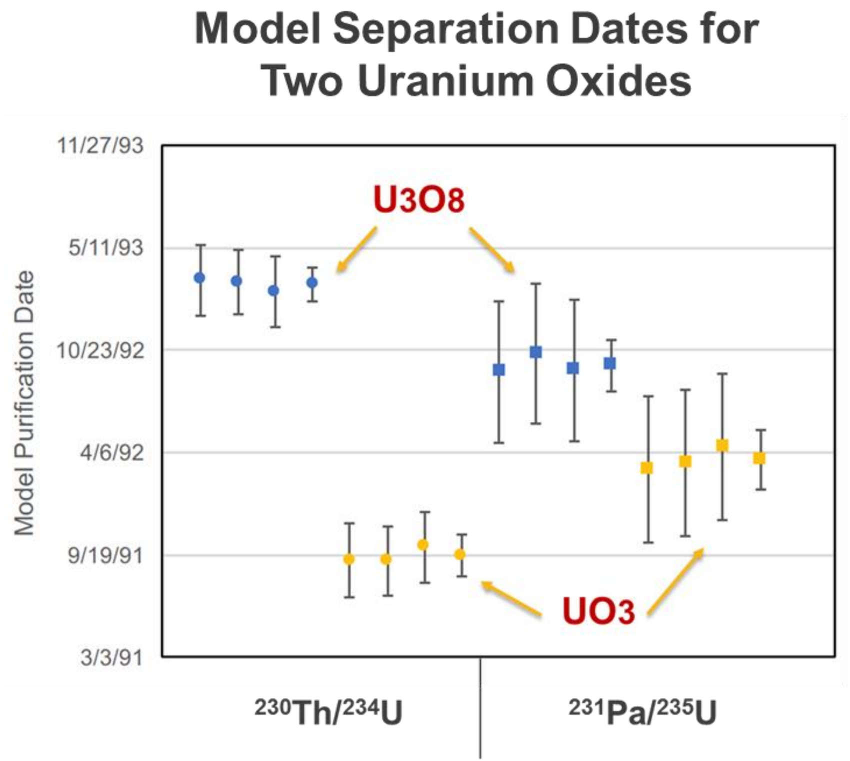
$\lambda_{230Th} = 9.16 \times 10^{-6}$

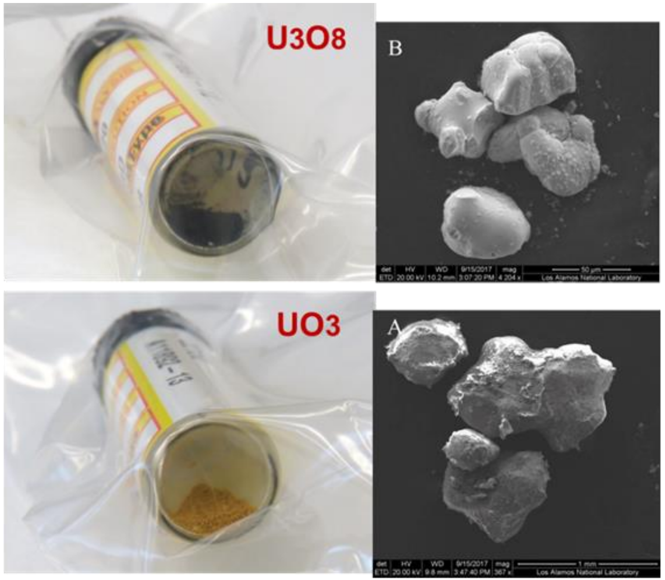
($T_{1/2}$ = 75,690 (230) years)

Cheng, H., Edwards, R.L., Hoff, J., Gallup. C.D., Richards, D.A., Asmerom, Y. (2000) The half-lives of uranium-234 and thorium-230. Chemical Geology, 169, 17-33.

The uncertainties expressed for the half lives of U-234 and Th-230 are expressed as 2σ expanded uncertainites. For error propagation purposes, the 1σ uncertianty should be used.

Recent Concordant Radiochronometry Measurements





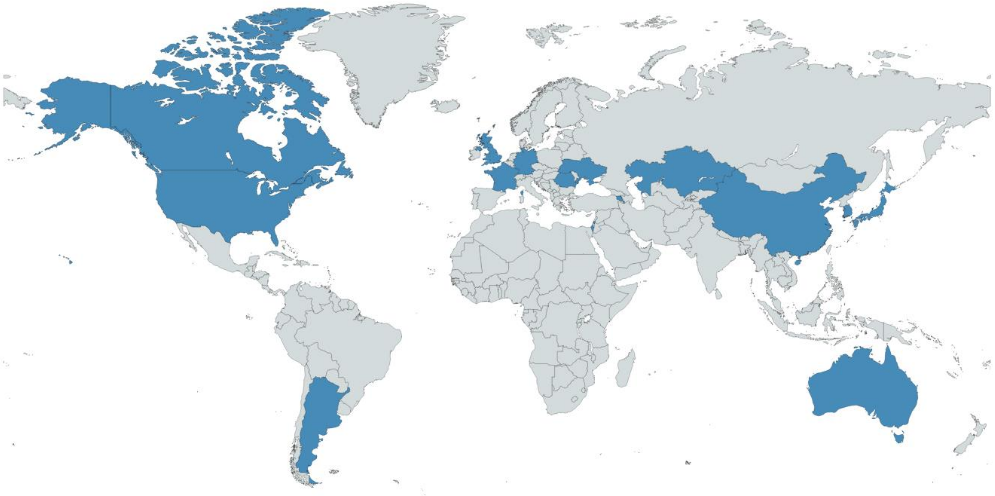
Two chronometers concordant within each material

Two materials differ in $^{230}Th/^{234}U$ age

Radiochronometry – A Collaborative History

- Partnerships initially grew out of collaborations developed through other programs: e.g. IAEA Network of Analytical Laboratories (NWAL)

- Global need to advance nuclear forensic signature science



- United States Department of Energy (US-DOE) collaborations in radiochronometry are currently supported by NA-213 Office of Nuclear Smuggling Detection and Deterrence

- Goal to globally strengthen the application of radiochronometry as a nuclear forensic signature to support investigations of nuclear material found out of regulatory control

- Armenia, Argentina, Australia, Canada, China, European Union, France, Japan, Kazakhstan, Republic of Korea, Romania, Ukraine, and the United Kingdom

Past – Capability Establishment, Collaborative Growth

Method Exchange → Interlaboratory Comparison → Technical Discussion → Publication → Scope Expansion

- US-DOE and China Institute of Atomic Energy
  - Initially exchanged methods for $^{230}Th/^{234}U$ radiochronometry
    Collaborative measurement of reference materials
    Collaborative publication in 2017
  - Continued collaboration for $^{231}Pa/^{235}U$ age dating
    Collaborative measurements of reference materials
    Collaborative publication in 2020
  - Advanced collaboration ongoing - multi-instrument radiochronometry study: MC-ICP-MS vs SC-ICP-MS

Bilateral meeting at CIAE in April 2017

- US-DOE and Korea Atomic Energy Research Institute
  - Initially exchanged methods for $^{230}Th/^{234}U$ radiochronometry
    Collaborative measurement of reference materials
    Collaborative report in 2019
  - Continued collaboration on plutonium age dating
    Collaborative measurements of reference materials
    Planned results in 2022

Bilateral meeting at KAERI in May 2019

Radiochronometry Outcomes

- Bi-lateral technical meetings to discuss radiochronometry observations, refine radiochemical purifications, and improve measurement techniques

- Publication of radiochemistry and mass spectrometry radiochronometry methods for the international community

- Publication of measured $^{230}Th/^{234}U$ and $^{231}Pa/^{235}U$ model ages for uranium certified reference materials

  – Comparative data for international community for the $^{231}Pa/^{235}U$ chronometer – helpful because there are no standards for quality control

- Publication of consensus model ages for plutonium isotopic certified reference materials

Applied Radiation and Isotopes 102 (2015) 81–86
Contents lists available at ScienceDirect
Applied Radiation and Isotopes
journal homepage: www.elsevier.com/locate/apradiso

Validation of reference materials for uranium radiochronometry in the frame of nuclear forensic investigations

Z. Varga[a,*], K. Mayer[a], C.E. Bonamici[b], A. Hubert[c], I. Hutcheon[d], W. Kinman[b], M. Kristo[d], F. Pointurier[c], K. Spencer[b], F. Stanley[b], R. Steiner[b], L. Tandon[b], R. Williams[d]

J Radioanal Nucl Chem
DOI 10.1007/s10967-017-5593-3

US-DOE and CIAE international cooperation in age-dating uranium standards

Kerri C. Treinen[1] · William S. Kinman[2] · Yan Chen[3] · Liuchao Zhu[3] · Annelise M. R. Cardon[2] · Robert E. Steiner[2] · Theresa M. Kayzar-Boggs[2] · Ross W. Williams[1] · Yong-Gang Zhao[3]

Journal of Radioanalytical and Nuclear Chemistry
https://doi.org/10.1007/s10967-020-07030-x

An interlaboratory collaboration to determine consensus $^{231}Pa/^{235}U$ model ages of a uranium certified reference material for nuclear forensics

Theresa M. Kayzar-Boggs[1] · Kerri C. Treinen[2] · Ayako Okubo[3] · Joanna S. Denton[1] · Amy M. Gaffney[2] · Martha M. Miller[2,4] · Robert E. Steiner[1] · Allison M. Wende[1] · Ross W. Williams[2]

analytical chemistry
Article
Cite This: Anal. Chem. 2019, 91, 11643–11652
pubs.acs.org/ac

Intercomparison of the Radio-Chronometric Ages of Plutonium-Certified Reference Materials with Distinct Isotopic Compositions

Kattathu Mathew,[*,†] Theresa Kayzar-Boggs,[‡] Zsolt Varga,[§] Amy Gaffney,[‖] Joanna Denton,[‡] James Fulwyler,[†] Katherine Garduno,[†] Andrew Gaunt,[‡] Jeremy Inglis,[‡] Russ Keller,[†] William Kinman,[‡] Dana Labotka,[†] Elmer Lujan,[†] Joel Maassen,[‡] Tara Mastren,[‡] Iain May,[‡] Klaus Mayer,[§] Adrian Nicholl,[§] Chelsea Ottenfeld,[†] Tashi Parsons-Davis,[‖] Donivan Porterfield,[†] Jung Rim,[†] John Rolison,[‖] Floyd Stanley,[†,¶] Rob Steiner,[‡] Lav Tandon,[†,∇] Mariam Thomas,[†] Richard Torres,[⊥] Kerri Treinen,[‖] Maria Wallenius,[§] Allison Wende,[‡] Ross Williams,[‖] and Josh Wimpenny[‖]

Los Alamos
NATIONAL LABORATORY

Present - Evolution of the Field

- Development of new certified reference materials

  ^{229}Th spike for isotope dilution mass spectrometry

  Concentration certified as mol / g solution

  Improvement in ^{230}Th/^{234}U model age uncertainties

  see Essex *et al.* 2018

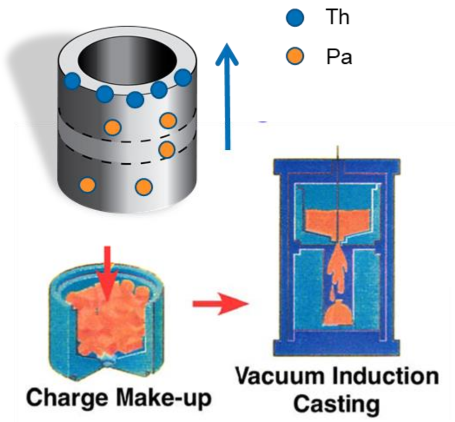
  ^{231}Pa standard for ^{233}Pa spike calibration

  Collaborative international effort: LLNL (USA), NPL (UK), NIST (USA), NRC Canada

  Faster, higher-precision spike calibration

  see Treinen *et al.* 2018 and Essex *et al.* 2019

Pa-231 unit as received at LANL



Uranium Metal Casting

Th often well-purified, migration to hot top of casting results in purification from U, ^{230}Th/^{234}U model ages are similar to casting dates

Pa remains in metal, not separated during casting, signature of feed material used for casting

UF_6 Storage

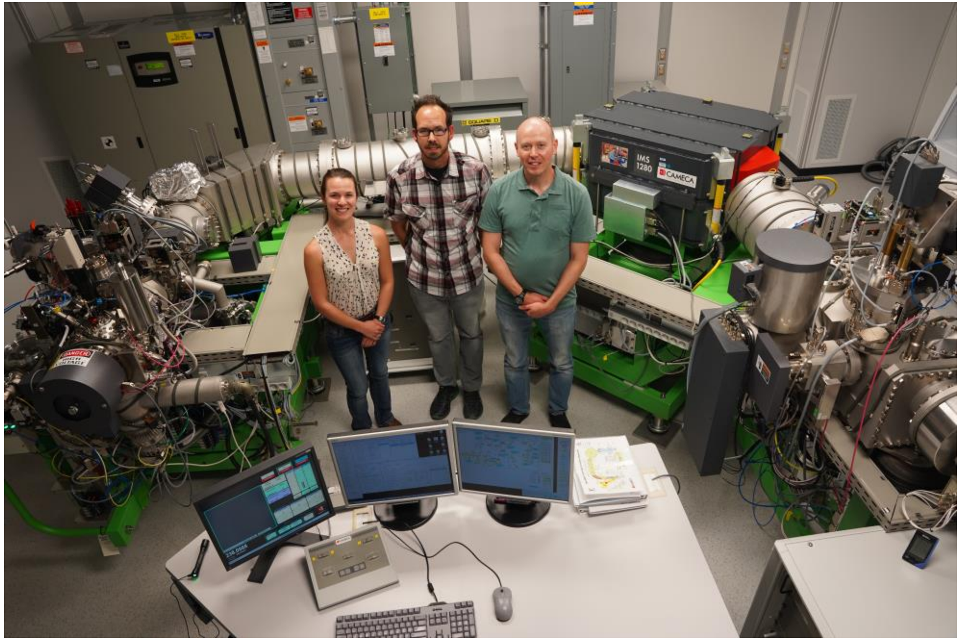
Migration of Th, Pa, Ac, and Ra into heel deposits formed by radiolysis and hydrolysis - UF_4, UO_2F_2

Sampling of heel deposits for radiochronometry

Spatially Resolved Analysis

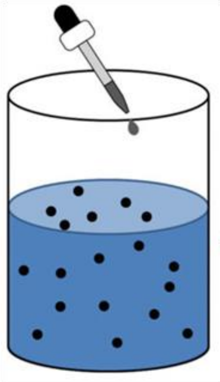
- Micro-scale characteristics are becoming useful to forensics

- Heterogeneity at the particle level
- Elemental associations
- Isotopic blending
- Production process
- Differentiate materials indistinguishable at the bulk level



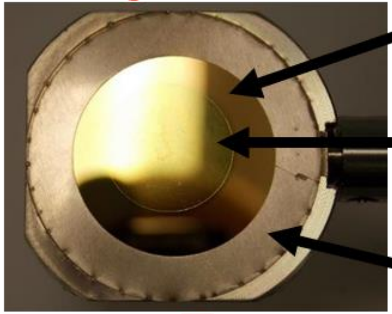
SIMS Sample Preparation

Sample



Suspension

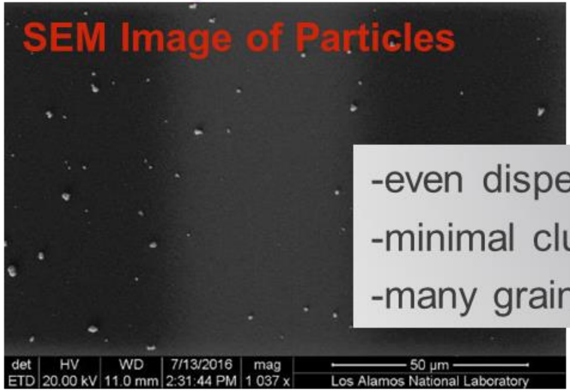
Casting



Au coated Si wafer

sample (staining)

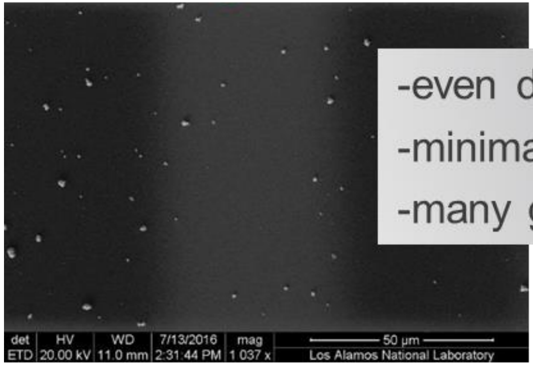
SIMS holder



-even dispersion
-minimal clumping
-many grains to analyze

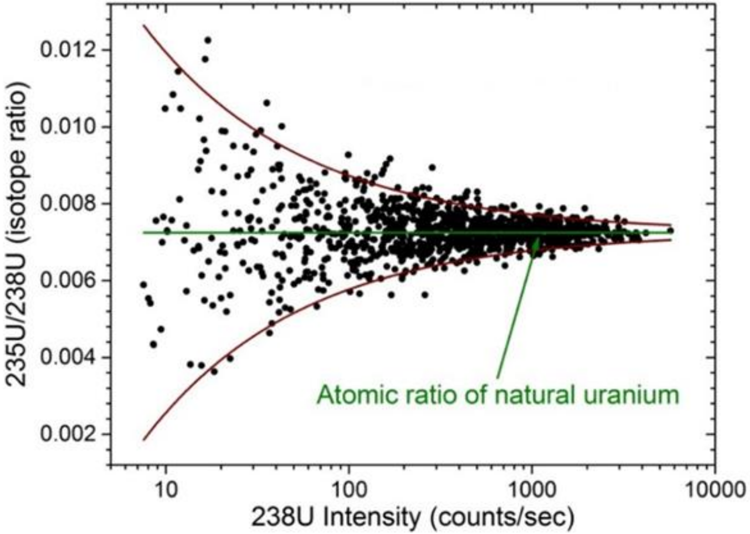
SIMS Measurements

SEM Image of Particles

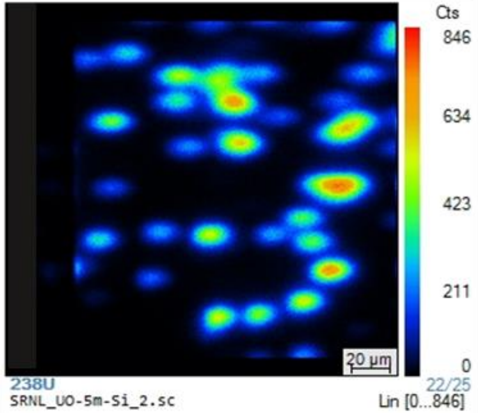


- -even dispersion
- -minimal clumping
- -many grains to analyze

$^{235}U/^{238}U$ Isotope Ratio Data

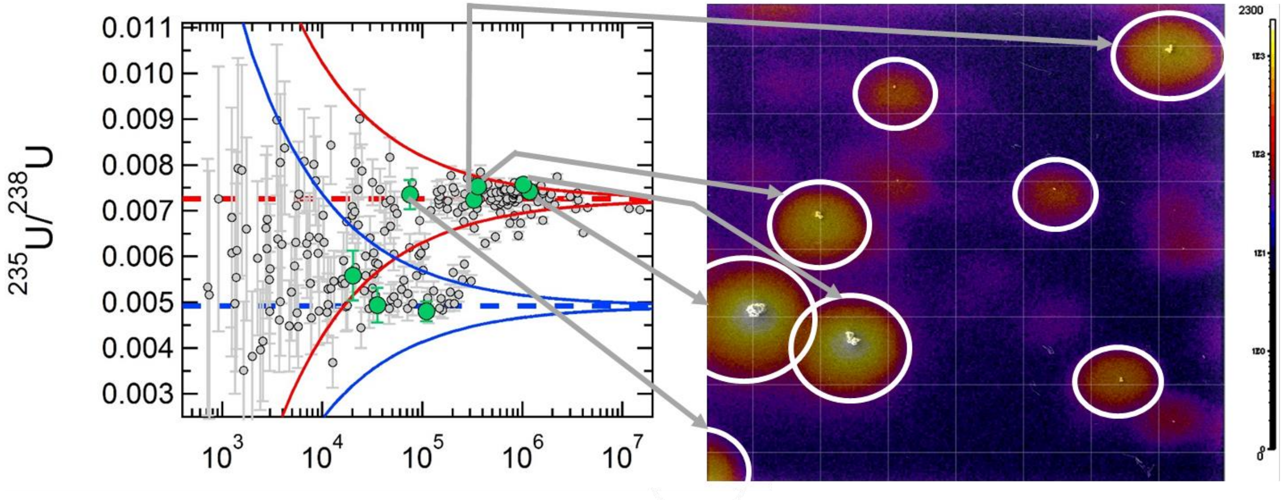


^{238}U Signal Intensity



Unfolding Mixtures of Uranium

Data for a Mixture of Natural Uranium and 0.005% Depleted Uranium



^{238}U counts

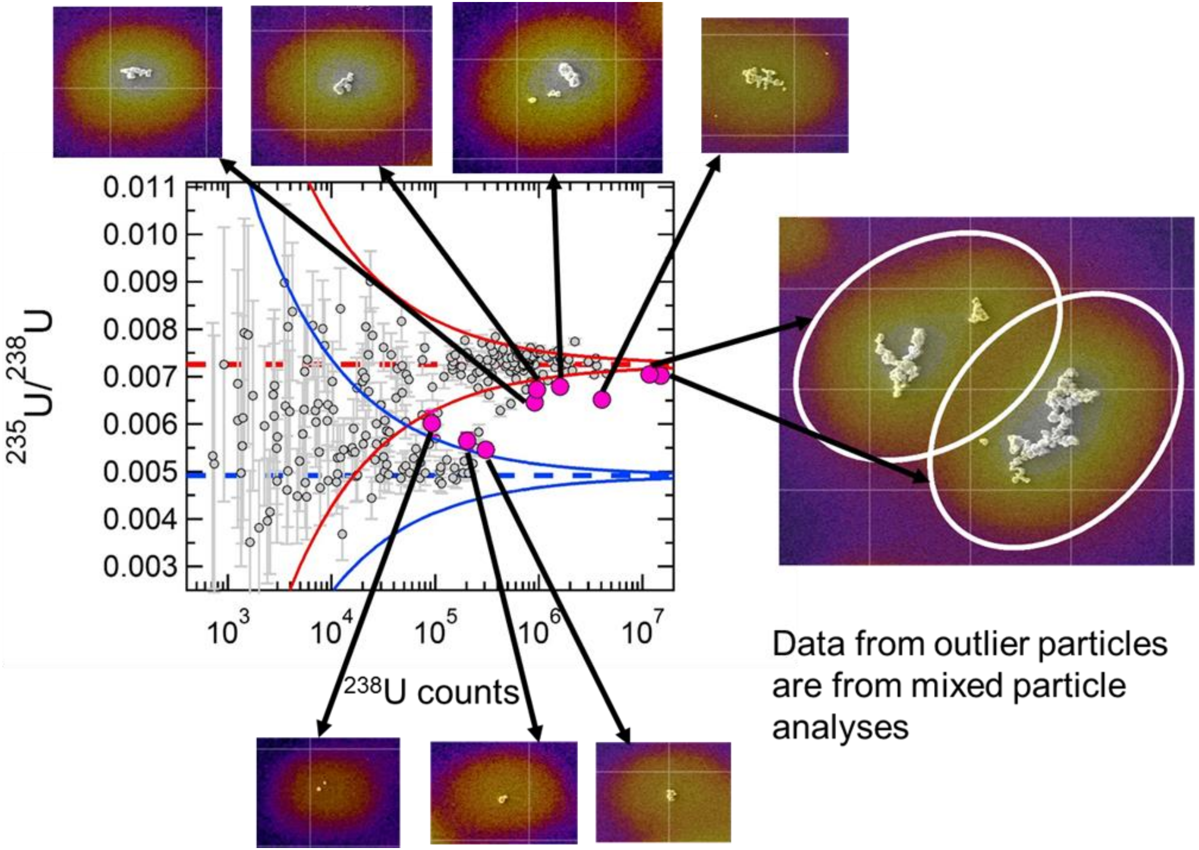
^{238}U image

- Using particle coordinates and reference grid interlaid with SEM image, particle data can be correlated with the exact particle
- The three small un-traced particles in the image are all from U005

Los Alamos NATIONAL LABORATORY

Identifying Particle Aggregates

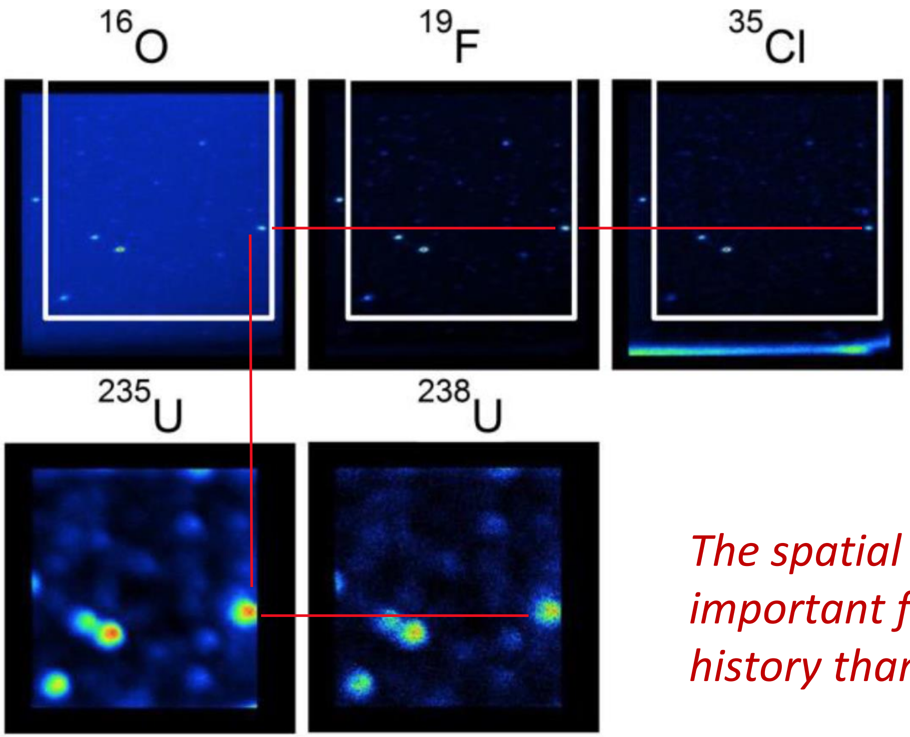
- SIMS data from aggregates of particles can be identified using SEM – SIMS images for each particle analyzed for isotopic composition



Data from outlier particles are from mixed particle analyses

Correlating Elements in Particles

UO_3 SIMS: Halogens and Light Isotopes
^{16}O, ^{19}F, ^{35}Cl with ^{235}U and ^{238}U



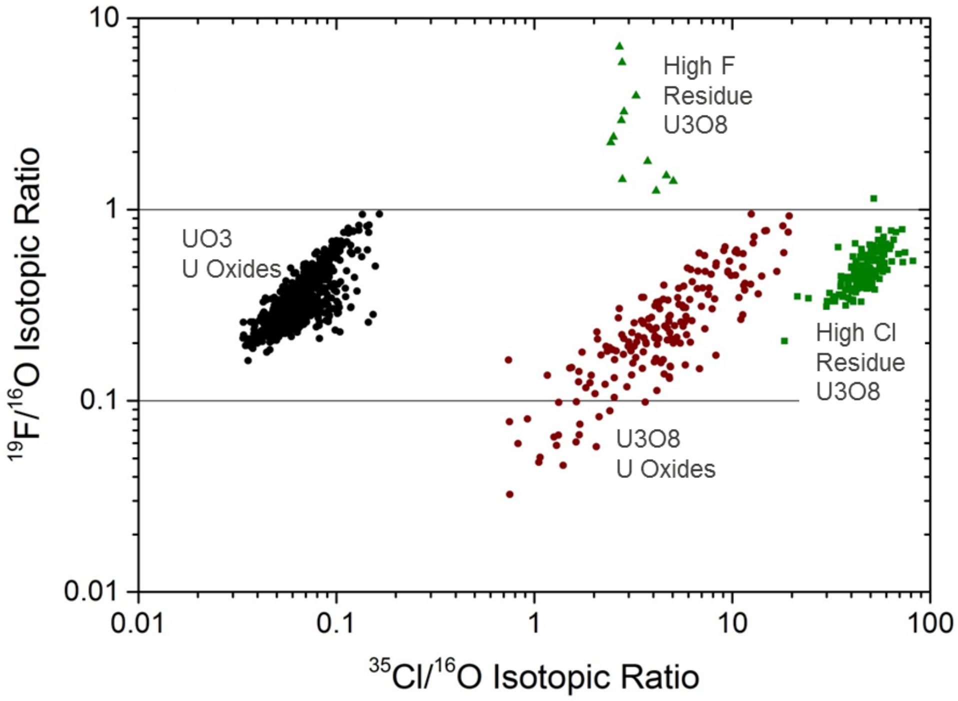
UO_3 and U_3O_8 sample

- UO_3 sample has F and Cl only associated with U in particles
- U_3O_8 sample contained F and Cl, including as discrete salt particles

The spatial distribution of impurities may be more important for identifying material and its process history than concentration

Identifying Particle Populations with Light Stable Isotopes

Distinct Populations of Particles in UO_3 and U_3O_8

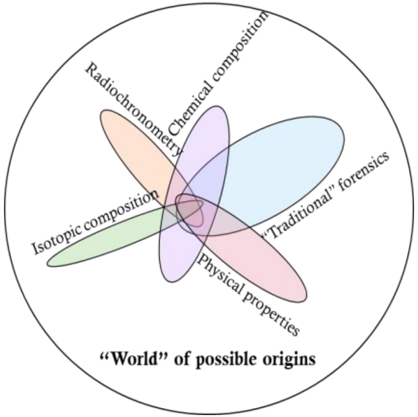


Combination of uranium and light stable isotope data shows promise for identifying different particle populations

Los Alamos NATIONAL LABORATORY

Nuclear Forensics Needs and Future Directions

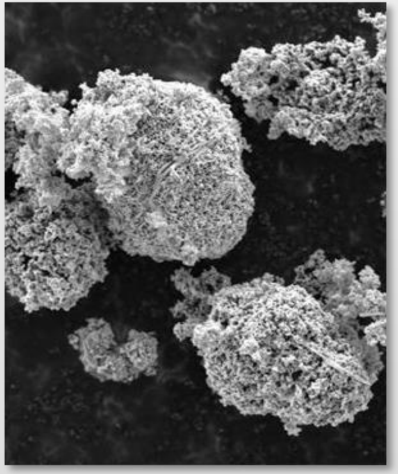
- Linking lab-based & in-field analysis
- Signature Research:
  - **Technique-based**
    - Morphology
    - Micro-signatures
    - Stable isotopes
    - Radiochronometry
  - **Material-based**
    - U ore & UOCs
    - Fuel pellets
    - U metals
    - Mixed materials
    - Materials contaminated with R/N



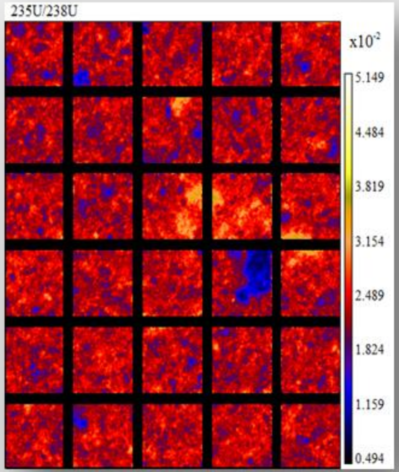
- NNFL Development
- Data evaluation & interpretation using machine learning and other tools

Signature Research

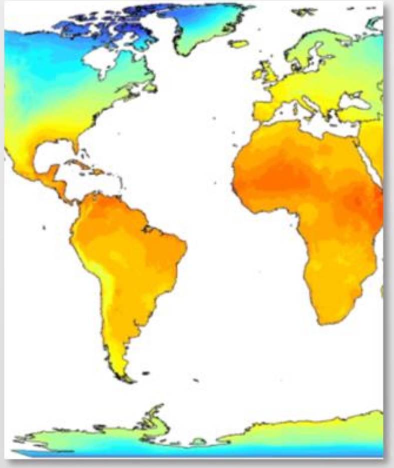
Morphology & Image Analysis



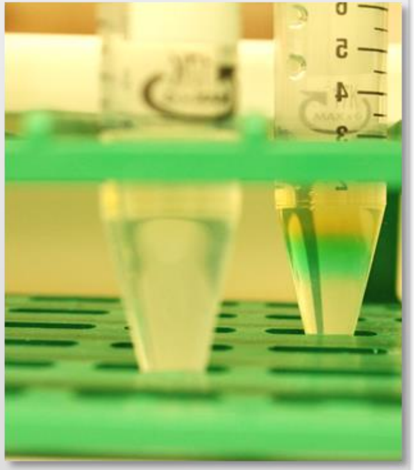
Spatially-resolved techniques



Stable isotopes



Age-dating & Multi-instrument approach



Linking material characteristics to processes, origin and pathways

Acknowledgements

U.S. Government's Nuclear Forensic Program

Department of Energy's Office of Nuclear Forensics (NA-83) and Office of Nuclear Smuggling Detection and Deterrence (NA-231)

Colleagues and collaborators

Greg Brennecka (LLNL)
Martin Robel (LLNL)
Rachel Lindvall (LLNL)
Mike Singleton (LLNL)
Quinn Shollenberger (LLNL)
John Rolison (LLNL)
Cheng Tarng (LLNL)
Matt Gonzales (LLNL)
Frank Wong (LLNL)
Erik Oerter (LLNL)
Tashi Parsons-Davis (LLNL)
Ashley Cocciadiferro (LLNL)
Jenny Matzel (LLNL)

Jerry Davydov (LANL)
Joanna Denton (LANL)
Mark Edwards (LANL)
Andrew Reinhard (LANL)
Rebecca Foley (LANL)
Ben Naes (LANL)
Kim Wurth (LANL)
Andrew Reinhard (LANL)
Allison Wende (LANL)
Mitzi Boswell (LANL)
Joel Maassen (LANL)
John Engel (LANL)
Azim Kara (LANL)

Mike Harris (LANL)
Lisa Hudston (LANL)
John Schwantes (PNNL)
Jodie Canaday (ANL)
Dick Pappas (NSDD)
Alina Smyslova (NSDD)
Erica Wolfe (NSDD)
Adam Stratz (NSDD)
Mansie Iyer (NSDD)
Liz Dallas (NSDD)
J. Joel Smith (NNSA-NA83)
Alison Goodsell (DOE)
Jim Blankenship (FBI)

Michael Curry (DOS)
Michael Wipper (DOS)
Jamie Gardner (DOS)

Thank You!

Questions?